The Diabatic Representation

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1 Example systems

Potential crossings are a very common phenomenon. Figure 1 shows some example systems and figure 2 shows the respective potentials.

Figure 1: (a) During the dissociation of the NaCl molecule, from a certain distance on it is preferable for the nuclei to be neutral because the Coulomb attraction of ions outweighs the (declining) gain made by forming an ionic bond.
(b) The desorption of an Atom from an ionic crystal using an STM/AFM tip leaving an F-centre behind. It is clear that the desorbed nucleus has undergone an electronic transition in the process.

a) Change of electronic state during dissociation of the NaCl molecule.

b) Desorbed atom leaves electron behind.

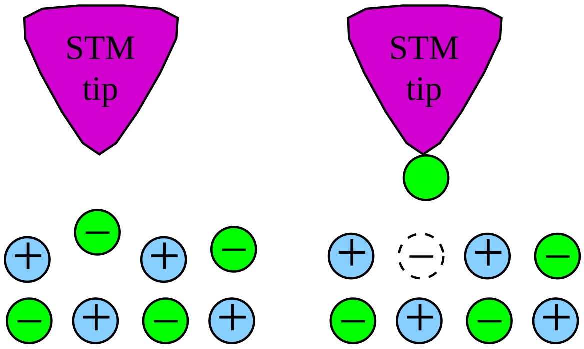
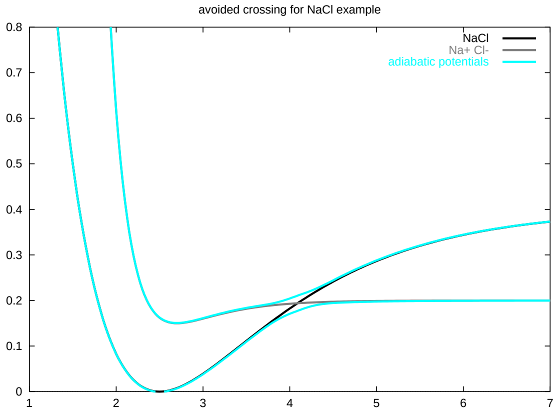
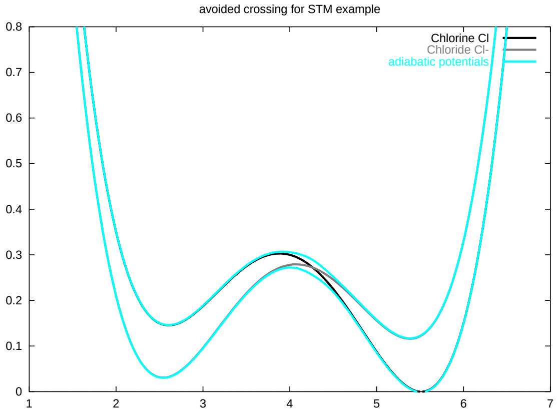


Figure 2: (a) A sketch of the adiabatic potentials for the ionic and atomic states of the NaCl molecule dissociation. The dark lines are the diabatic potentials for a certain electronic state, the light lines are the eigenvalues of the Hamilton operator - the adiabatic potential lines - which avoid each other.
(b) A speculation on adiabatic potentials for the desorption of a Chlorine atom/Chloride ion from an NaCl surface. On the right-hand side - on the surface of the crystal, it is more preferable for the Chlorine to bind an electron to itself. Calculations by Peter Sushko predict that the desorbed atom leaves about three quarters of the electron behind and gives the rest to the conducting silicon tip.



(a) adiabatic



(b) adiabatic

2 Problems connected to potential crossings

There are several ways to approach the problem of potential crossings.

2.1 Avoided crossings (as known from textbooks)

Starting from a system with hypothetical potential lines that cross each other, assuming a certain coupling, perturbation theory proves that the energy levels will split under the coupling as perturbation and adiabatic potentials avoiding each other result.

2.2 Quantum-chemical approach

(Using adiabatic potentials.) The adiabatic potentials are calculated and, often using configuration interaction, non-adiabaticity operators are derived to quantify the coupling rates.

2.3 Quantum-physical approach

(Using diabatic potentials.) To simulate the dynamic behaviour of the system or to find transition rates between electronic energy levels, one tries to represent the coupling elements between the states as non-diagonal potential matrix elements. This has the advantage of being numerically benevolent. The rest of this text shall deal with this problem.

3 Adiabatic Representation

Consider a wave function

$$\psi = \sum \varphi_i^{(\mathrm{a})}(\mathbf{r},\mathbf{R})\,\chi_i^{(\mathrm{a})}(\mathbf{R},t) \tag{1}$$

where $\varphi_i^{(\mathrm{a})}$ are adiabatic electronic wave functions and $\chi_i^{(\mathrm{a})}$ are adiabatic nuclear wave functions, $\mathbf{r}$ and $\mathbf{R}$ are the electronic and nuclear coordinates and t is time.

Assuming the electronic wave functions do *not* depend on the nuclear coordinates invokes the crude adiabatic approximation. It often leads to very slow convergence of the expansion (1).

In free space the complete system Hamiltonian can be written as

$$H = -\frac{\hbar^2}{2\mu}\nabla_{\mathrm{nuc}}^2 + H_{\mathrm{el}} = T_{\mathrm{nuc}} + H_{\mathrm{el}} \tag{2}$$

where T_{nuc} is the nuclear kinetic energy, ∇_{nuc} the nuclear gradient (mass-scaled) and H_{el} contains all interaction and the electronic kinetic energies.

4 Coupled Equations - Non-Adiabatic Representation

The left-hand side of the Schrödinger equation can then be written as:

$$\begin{aligned}
H\psi &= (T_{\mathrm{nuc}} + H_{\mathrm{el}})\sum \varphi_i^{(\mathrm{a})}\chi_i^{(\mathrm{a})} && (3)\\
&= -\frac{\hbar^2}{2\mu}\sum \nabla_{\mathrm{nuc}}^2\left(\varphi_i^{(\mathrm{a})}\chi_i^{(\mathrm{a})}\right) + \sum H_{\mathrm{el}}\varphi_i^{(\mathrm{a})}\chi_i^{(\mathrm{a})} && (4)\\
&= -\frac{\hbar^2}{2\mu}\sum\Big[\left(\nabla_{\mathrm{nuc}}^2\varphi_i^{(\mathrm{a})}\right)\chi_i^{(\mathrm{a})} + 2\left(\nabla_{\mathrm{nuc}}\varphi_i^{(\mathrm{a})}\right)\left(\nabla_{\mathrm{nuc}}\chi_i^{(\mathrm{a})}\right)\\
&\qquad + \varphi_i^{(\mathrm{a})}\left(\nabla_{\mathrm{nuc}}^2\chi_i^{(\mathrm{a})}\right)\Big] + \sum H_{\mathrm{el}}\varphi_i^{(\mathrm{a})}\chi_i^{(\mathrm{a})} && (5)
\end{aligned}$$

Let $\left\{\varphi_i^{(\mathrm{a})}\right\}$ be an orthonormal complete set of eigenfunctions of H_{el} over the electronic coordinates

$$\begin{aligned}
\langle\varphi_j(\mathbf{r},\mathbf{R})|\varphi_i(\mathbf{r},\mathbf{R})\rangle_{\mathrm{el}} &= \delta_{ji}\,,\ \sum|\varphi_k\rangle\langle\varphi_k| = 1, && (6)\\
H_{\mathrm{el}}\varphi_i(\mathbf{r},\mathbf{R}) &= V_i(\mathbf{R})\,\varphi_i(\mathbf{r},\mathbf{R})\,, && (7)
\end{aligned}$$

multiply $\left\langle\varphi_j^{(\mathrm{a})}\right|$ from the left:

$$\left\langle\varphi_j^{(\mathrm{a})}\left|H\right|\psi\right\rangle = \left[V_j^{(\mathrm{a})} + T_{\mathrm{nuc}} + K_{jj}^{(\mathrm{a})}\right]\chi_j^{(\mathrm{a})} + \sum_{i\neq j} K_{ji}^{(\mathrm{a})}\chi_i^{(\mathrm{a})} \tag{8}$$

with

$$K_{ji}^{(\mathrm{a})} = -\frac{\hbar^2}{2\mu}\left[\left\langle \varphi_j^{(\mathrm{a})} | \nabla^2_{\mathrm{nuc}} \varphi_i^{(\mathrm{a})} \right\rangle + 2\left\langle \varphi_j^{(\mathrm{a})} | \nabla_{\mathrm{nuc}} \varphi_i^{(\mathrm{a})} \right\rangle \nabla_{\mathrm{nuc}}\right]. \tag{9}$$

If ψ is an eigenvector of the Hamiltonian then $H\psi = E\psi$ and hence

$$\left\langle \varphi_j^{(\mathrm{a})} |H| \psi \right\rangle = E\left\langle \varphi_j^{(\mathrm{a})} | \psi \right\rangle = E\sum \delta_{ji}\chi_i^{(\mathrm{a})} = E\chi_j^{(\mathrm{a})} \tag{10}$$

and the steady-state Schrödinger equation is

$$\left[V_j^{(\mathrm{a})} + T_{\mathrm{nuc}} + K_{jj}^{(\mathrm{a})} - E\right]\chi_j^{(\mathrm{a})} + \sum K_{ji}^{(\mathrm{a})}\chi_i^{(\mathrm{a})} = 0 \tag{11}$$

or, in matrix formulation,

$$\left[\mathbf{V}^{(\mathrm{a})} + \mathbf{T}_{\mathrm{nuc}} + \mathbf{K}^{(\mathrm{a})} - E\right]\chi^{(\mathrm{a})} = 0. \tag{12}$$

Accordingly, the time-dependent Schrödinger equation is

$$i\hbar\dot{\chi}^{(\mathrm{a})} = \left[\mathbf{V}^{(\mathrm{a})} + \mathbf{T}_{\mathrm{nuc}} + \mathbf{K}^{(\mathrm{a})}\right]\chi^{(\mathrm{a})}. \tag{13}$$

Here, $\mathbf{V}^{(\mathrm{a})}$ is a diagonal Matrix and the kinetic coupling operator $\mathbf{K}^{(\mathrm{a})}$ is generally a fully occupied matrix and $\chi^{(\mathrm{a})}$ is the vector of adiabatic nuclear states.

Apart from the kinetic coupling terms $\mathbf{K}^{(\mathrm{a})}$, this equation (12) looks like a simple Hamiltonian Schrödinger equation for the nuclear wave functions. Accordingly, by neglecting the kinetic coupling terms between the electronic and nuclear coordinates $\mathbf{K}^{(\mathrm{a})}$, easy to solve differential equations for the nuclear coordinates are obtained. This neglect is called *Born-Oppenheimer approximation.*

Equation (12) can be rearranged using the notation

$$\begin{aligned}
T_{ji}^{(1)} &= \langle \varphi_j | \nabla_{\mathrm{nuc}} \varphi_i \rangle & (14)\\
T_{ji}^{(2)} &= \left\langle \varphi_j | \nabla^2_{\mathrm{nuc}} \varphi_i \right\rangle, \text{ so that} & (15)\\
\to K_{ji}^{(\mathrm{a})} &= -\frac{\hbar^2}{2\mu}\left(2T_{ji}^{(1)}\nabla_{\mathrm{nuc}} + T_{ji}^{(2)}\right), & (16)\\
\Rightarrow \quad 0 &= \left[-\frac{\hbar^2}{2\mu}\left(\nabla + \mathbf{T}^{(1)}\right)^2 + \mathbf{V}^{(\mathrm{a})} - E\right]\chi^{(\mathrm{a})} & (17)
\end{aligned}$$

This can be shown by looking at the elements of the matrix $\left(\nabla + \mathbf{T}^{(1)}\right)^2$:

$$\begin{aligned}
\left(\nabla + \mathbf{T}^{(1)}\right)^2_{ji} &= \left(\nabla^2 + \mathbf{T}^{(1)}\nabla + \nabla\mathbf{T}^{(1)} + \mathbf{T}^{(1)2}\right)_{ji} & (18)\\
&= \nabla^2 + 2\underbrace{\langle \varphi_j | \nabla\varphi_i \rangle}_{T_{ji}^{(1)}}\nabla + \underbrace{\left\langle \varphi_j | \nabla^2\varphi_i \right\rangle}_{T_{ji}^{(2)}}\\
&\quad + \langle \nabla\varphi_j | \nabla\varphi_i \rangle + \sum_k \langle \varphi_j | \nabla\varphi_k \rangle \langle \varphi_k | \nabla\varphi_i \rangle & (19)
\end{aligned}$$

Now

$$\nabla\langle \varphi_j | \varphi_k \rangle = \langle \nabla\varphi_j | \varphi_k \rangle + \langle \varphi_j | \nabla\varphi_k \rangle = \nabla\delta_{jk} = 0,$$

hence

$$\langle \varphi_j | \nabla\varphi_k \rangle = -\langle \nabla\varphi_j | \varphi_k \rangle \tag{20}$$

$\mathbf{T}^{(1)}$ is antihermitean. Since $\sum_k |\varphi_k\rangle\langle\varphi_k| = 1$, this means that the last two terms in eq. (19) cancel.

$$\text{Corollary: } \left(\nabla\mathbf{T}^{(1)}\right) = \mathbf{T}^{(2)} - \mathbf{T}^{(1)2}. \tag{21}$$

$\left(\nabla + \mathbf{T}^{(1)}\right)^2$ is sometimes called “dressed kinetic energy operator”.[4,5]

In practice, a group of states is selected, among which coupling is taken into account explicitly:

$$\left[-\frac{\hbar^2}{2\mu}\left(\nabla + \mathbf{T}^{(1,\mathrm{g})}\right)^2 + \mathbf{T}^{(3,\mathrm{g})} - E\right]\chi^{(\mathrm{a})} = 0\,, \tag{22}$$

where $\mathbf{T}^{(3,\mathrm{g})}$ denotes the term formed by the potentials and the part of the last term in eq. (19) missing in $\left(\nabla + \mathbf{T}^{(1,\mathrm{g})}\right)^2$. Using the projector on the selected group of states $\hat{P}_{\mathrm{g}}$, this is

$$T_{ji}^{(3,\mathrm{g})}(\mathbf{R}) = V_i^{(\mathrm{g})}(\mathbf{R})\,\delta_{ij} + \frac{\hbar^2}{2\mu}\left\langle \nabla\varphi_j \left| \left(1 - \hat{P}_{\mathrm{g}}\right) \right| \nabla\varphi_i \right\rangle. \tag{23}$$

This term is called “dressed potential energy”.

Starting from the eigenvalue equation for the electronic Hamiltonian

$$H_{\mathrm{el}}\varphi_i(\mathbf{r},\mathbf{R}) = V_i(\mathbf{R})\,\varphi_i(\mathbf{r},\mathbf{R}), \tag{24}$$

the following relation can be extracted for the derivative coupling $T_{ji}^{(1)}$:

$$\begin{aligned}
(\nabla_{\mathrm{nuc}}H_{\mathrm{el}})\,\varphi_i + H_{\mathrm{el}}\,(\nabla_{\mathrm{nuc}}\varphi_i) &= (\nabla_{\mathrm{nuc}}V_i)\,\varphi_i + V_i\,(\nabla_{\mathrm{nuc}}\varphi_i) && (25)\\
\langle\varphi_j\,|(\nabla H_{\mathrm{el}})|\,\varphi_i\rangle + \langle\varphi_j\,|H_{\mathrm{el}}|\,\nabla\varphi_i\rangle & \\
= \langle\varphi_j\,|(\nabla V_i(\mathbf{R}))|\,\varphi_i\rangle_{\mathrm{el}} &+ \langle\varphi_j\,|V_i|\,\nabla\varphi_i\rangle && (26)\\
\langle\varphi_j\,|(\nabla H_{\mathrm{el}})|\,\varphi_i\rangle + V_j\,\langle\varphi_j|\nabla\varphi_i\rangle & \\
= (\nabla V_i(\mathbf{R}))\,\delta_{ji} &+ V_i\,\langle\varphi_j|\nabla\varphi_i\rangle && (27)\\
\rightarrow\quad T_{ji}^{(1)} = \langle\varphi_j|\nabla_{\mathrm{nuc}}\varphi_i\rangle &= \frac{\langle\varphi_j\,|(\nabla_{\mathrm{nuc}}H_{\mathrm{el}})|\,\varphi_i\rangle_{\mathrm{el}}}{V_i(\mathbf{R}) - V_j(\mathbf{R})}. && (28)
\end{aligned}$$

The denominator becomes small close to avoided crossings, so that the Born-Oppenheimer approximation breaks down in such regions, as the coupling terms become large compared to the elements of $V^{(\mathrm{a})}$. This problem is dealt with in the following.

5 Diabatic Representation[1]

A unitary transformation $\mathbf{U}(\mathbf{R})$ in the vector space of electronic states does not change the wave function ψ:

$$\begin{aligned}
\psi &= \sum\varphi_i^{(\mathrm{a})}\chi_i^{(\mathrm{a})} = \varphi^{a+}\chi^{(\mathrm{a})} = \varphi^{a+}\mathbf{U}\cdot\mathbf{U}^{+}\chi^{(\mathrm{a})} && (29)\\
&= \left(\mathbf{U}^{+}\varphi^{a}\right)^{+}\left(\mathbf{U}^{+}\chi^{(\mathrm{a})}\right) = \varphi^{d+}\chi^{(\mathrm{d})}. && (30)
\end{aligned}$$

The wave functions obtained by application of the unitary transformation $\mathbf{U}^{+}$ are denoted $\varphi^{(\mathrm{d})}$ and $\chi^{(\mathrm{d})}$, respectively.

To obtain the Schrödinger equation for the transformed wave functions, apply the operators $\mathbf{T}_{\mathrm{nuc}}$ and $\mathbf{K}^{(\mathrm{a})}$ to the adiabatic nuclear wave function $\chi^{(\mathrm{a})} = \mathbf{U}\chi^{(\mathrm{d})}$:

$$\begin{aligned}
\mathbf{T}_{\mathrm{nuc}}\chi^{(\mathrm{a})} &= -\frac{\hbar^2}{2\mu}\nabla_{\mathrm{nuc}}^2\left(\mathbf{U}\chi^{(\mathrm{d})}\right) && (31)\\
&= -\frac{\hbar^2}{2\mu}\left[\left(\nabla^2\mathbf{U}\right)\chi^{(\mathrm{d})} + 2\left(\nabla\mathbf{U}\right)\left(\nabla\chi^{d}\right) + \mathbf{U}\left(\nabla^2\chi^{d}\right)\right] && (32)\\
&= -\frac{\hbar^2}{2\mu}\left[\left(\nabla^2\mathbf{U}\right) + 2\left(\nabla\mathbf{U}\right)\nabla + \mathbf{U}\nabla^2\right]\chi^{(\mathrm{d})} && (33)
\end{aligned}$$

The kinetic coupling term is

$$\begin{aligned}
\mathbf{K}^{(\mathrm{a})}\chi^{(\mathrm{a})} &= -\frac{\hbar^2}{2\mu}\left[2\mathbf{T}^{(1)}\nabla + \mathbf{T}^{(2)}\right]\chi^{(\mathrm{a})} && (34)\\
&= -\frac{\hbar^2}{2\mu}\left[2\mathbf{T}^{(1)}\left(\nabla\mathbf{U}\right) + 2\mathbf{T}^{(1)}\mathbf{U}\nabla + \mathbf{T}^{(2)}\mathbf{U}\right]\chi^{(\mathrm{d})} && (35)
\end{aligned}$$

So the Schrödinger equation is

$$\begin{aligned}
0 &= \left[\mathbf{V}^{(\mathrm{a})} - E + \left(\mathbf{T}_{\mathrm{nuc}} + \mathbf{K}^{(\mathrm{a})}\right)\right]\mathbf{U}\chi^{(\mathrm{d})} && (36)\\
&= \left[\left(\mathbf{V}^{(\mathrm{a})} - E\right)\mathbf{U} - \frac{\hbar^2}{2\mu}\left(\nabla^2\mathbf{U} + 2\mathbf{T}^{(1)}\left(\nabla\mathbf{U}\right) + \mathbf{T}^{(2)}\mathbf{U}\right)\right.\\
&\quad\left.-\frac{\hbar^2}{2\mu}2\left(\nabla\mathbf{U} + \mathbf{T}^{(1)}\mathbf{U}\right)\nabla - \frac{\hbar^2}{2\mu}\mathbf{U}\nabla^2\right]\chi^{(\mathrm{d})}. && (37)
\end{aligned}$$

Apart from being unitary, $\mathbf{U}$ has not been restricted yet, so at this point it can be chosen such as to solve the differential equation

$$\nabla\mathbf{U} + \mathbf{T}^{(1)}\mathbf{U} = 0. \tag{38}$$

This makes the coefficient of the first derivative zero.

If $\left\{\varphi_n^{(\mathrm{a})}\right\}$ is a complete set, the term $2\mathbf{T}^{(1)}\left(\nabla\mathbf{U}\right) + 2\mathbf{T}^{(2)}\mathbf{U} + \nabla^2\mathbf{U}$ becomes zero as well.

proof: The first derivative of equation (38) is

$$\nabla^2\mathbf{U} + \left(\nabla\mathbf{T}^{(1)}\right)\mathbf{U} + \mathbf{T}^{(1)}\nabla\mathbf{U} = 0 \tag{39}$$

If $\left\{\varphi_n^{(\mathrm{a})}\right\}$ **is a complete set**, $\left(\nabla\mathbf{T}^{(1)}\right) = \mathbf{T}^{(2)} - \mathbf{T}^{(1)2}$, so (39) takes the form

$$\nabla^2\mathbf{U} + \mathbf{T}^{(2)}\mathbf{U} - \mathbf{T}^{(1)2}\mathbf{U} + \mathbf{T}^{(1)}\nabla\mathbf{U} = 0. \tag{40}$$

On the other hand, application of $\mathbf{T}^{(1)}$ to the given restricting equation (38) gives $-\mathbf{T}^{(1)2}\mathbf{U} = \mathbf{T}^{(1)}\nabla\mathbf{U}$ so finally

$$\nabla^2\mathbf{U} + 2\mathbf{T}^{(1)}\nabla\mathbf{U} + \mathbf{T}^{(2)}\mathbf{U} = 0, \tag{41}$$

which is the desired result.

So eventually the Schrödinger equation simplifies to

$$\left[\left(\mathbf{V}^{(\mathrm{a})} - E\right)\mathbf{U} - \frac{\hbar^2}{2\mu}\mathbf{U}\nabla^2\right]\chi^{(\mathrm{d})} = 0. \tag{42}$$

Applying $\mathbf{U}^{+}$ from the left gives

$$\left[\left(\mathbf{V}^{(\mathrm{d})} - E\right) - \frac{\hbar^2}{2\mu}\nabla^2\right]\chi^{(\mathrm{d})} = 0 \quad \text{with } \mathbf{V}^{(\mathrm{d})} = \mathbf{U}^{+}\mathbf{V}^{(\mathrm{a})}\mathbf{U} \tag{43}$$

which has the form of a simple Schrödinger equation

$$\left[\left(\mathbf{V}^{(\mathrm{d})} - E\right) + \mathbf{T}_{\mathrm{nuc}}\right]\chi^{(\mathrm{d})} = 0 \tag{44}$$

or, for the time-dependent case,

$$i\hbar\dot{\chi}^{(\mathrm{d})} = \left[\mathbf{V}^{(\mathrm{d})} + \mathbf{T}_{\mathrm{nuc}}\right]\chi^{(\mathrm{d})} = 0. \tag{45}$$

In this equation, however, the potential $\mathbf{V}^{(\mathrm{d})}$ is **not** a diagonal matrix. The kinetic coupling elements, which have been extinguished are reflected in the coupling of the electronic states via the non-diagonal elements of the potential matrix. The difficulties of solving the Schrödinger equation were moved from the kinetic coupling terms $\mathbf{T}^{(1/2)}$ to the non-diagonal elements of the potential and to the calculation of the transformation matrix itself. As $\mathbf{U}$ is unitary, all expectation values of observables stay the same under the diabatic transformation.

6 Structure of the matrix $\mathbf{T}^{(1)}$

$\mathbf{T}^{(1)}$ is antihermitean (20) and approximately zero sufficiently far away from crossings. For an avoided crossing mediating an allowed transition between $\varphi_i^{(\mathrm{a})}$ and $\varphi_j^{(\mathrm{a})}$, $T_{ij}^{(1)}$ is often of Lorentzian shape:

$$T_{ij}^{(1)} = \frac{\Gamma_{ij}/4}{\left[\mathbf{R} - \mathbf{R}_{ij}^{c}\right]^2 + \Gamma_{ij}^2/4},$$

where

- Γ_{ij} is the full width at half maximum of an avoided crossing and
- $\mathbf{R}_{ij}^{c}$ is the space coordinate of the avoided crossing.

7 Solution of equation (38)

As matrices are generally non-commuting, the formal solution of equation (38) is

$$\mathbf{U}(\mathbf{R}) = \mathbf{U}(\mathbf{R}_0) \cdot \hat{R} \cdot e^{-\int_{\gamma} \mathbf{T}^{(1)}(\mathbf{R}')d\mathbf{R}'}, \tag{46}$$

along some path $\gamma : \mathbf{R}_0 \rightarrow \mathbf{R}$, where $\hat{R}$ is the space ordering operator with:

$$\hat{R}\left\{A_1(\mathbf{R}_1) \cdot A_2(\mathbf{R}_2)\right\} = \begin{cases} A_1(\mathbf{R}_1) \cdot A_2(\mathbf{R}_2), & \text{if } \gamma^{-1}(\mathbf{R}_1) \leq \gamma^{-1}(\mathbf{R}_2), \\ A_2(\mathbf{R}_2) \cdot A_1(\mathbf{R}_2), & \text{otherwise.} \end{cases} \tag{47}$$

Accordingly, using the definition is the simplest way to approximate $\mathbf{U}$. Let $\Delta\mathbf{R} = \frac{\mathbf{R}-\mathbf{R}_0}{M}$ then[2]

$$-\int\limits_{\gamma} \mathbf{T}^{(1)}(\mathbf{R}')\,d\mathbf{R} \approx -\sum_{n=0}^{M-1} \mathbf{T}^{(1)}(\mathbf{R}_0 + n\Delta\mathbf{R})\,\Delta\mathbf{R} \tag{48}$$

$$\mathbf{U}(\mathbf{R}) \approx \mathbf{U}(\mathbf{R}_0) \prod_{n=0}^{M-1} e^{-\mathbf{T}^{(1)}(\mathbf{R}_0+n\Delta\mathbf{R})\Delta\mathbf{R}} \tag{49}$$

The order of the exponential terms is kept in the calculation, so the space order operator is applied.

- Choose $\mathbf{R}_0$ far away from any avoided crossing, so $U(\mathbf{R}_0)$ can be set to unity.
- Calculate each $e^{-\mathbf{T}^{(1)}(\mathbf{R}_0+n\cdot\Delta\mathbf{R})\Delta\mathbf{R}}$ by diagonalising $T^{(1)}(\mathbf{R}_0 + n\Delta R)\,\Delta\mathbf{R}$.

Example: two electronic states. $\mathbf{T}^{(1)}$ is antihermitian, so it only has one independent element: $T_{12}^{(1)}$. Let $A_{12} = -\int\limits_{\gamma} T_{12}^{(1)}(\mathbf{R}')\,d\mathbf{R}'$. Then the eigenvalues of the matrix $\mathbf{A}$ are $\lambda_{1/2} = \pm i\alpha$ with $\alpha = |A_{12}|$. Calculation of the eigenvectors gives

$$\mathbf{U}(\mathbf{R}) = \frac{1}{2}\begin{pmatrix} 1 & 1 \\ i & -i \end{pmatrix}\begin{pmatrix} e^{i\alpha} & 0 \\ 0 & e^{-i\alpha} \end{pmatrix}\begin{pmatrix} 1 & -i \\ 1 & i \end{pmatrix} \tag{50}$$

$$= \begin{pmatrix} \cos\alpha(\mathbf{R}) & \sin\alpha_{12}(\mathbf{R}) \\ -\sin\alpha(\mathbf{R}) & \cos\alpha(\mathbf{R}) \end{pmatrix} \tag{51}$$

Hence $\alpha(\mathbf{R})$ is called mixing angle.

In case $T_{12}^{(1)}$ in the direction of some path can be approximated by a Lorentzian

$$T_{12}^{(1)} \approx \frac{\Gamma_{12}/4}{\left[\mathbf{R} - \mathbf{R}_{12}^{c}\right]^2 + \Gamma_{12}^2/4} \tag{52}$$

the mixing angle can be found analytically[3] to be

$$\alpha = -\frac{1}{2}\arctan\left[\frac{2\left|\mathbf{R} - \mathbf{R}_{12}^{c}\right|}{\Gamma_{12}}\right] - \frac{\pi}{4}. \tag{53}$$

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